Properties of Cu in ZnO: theory explains experiment

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Cu in ZnO is one of the most intensively investigated TM dopant, particularly after the discovery of the robust room temperature ferromagnetism in ZnO:Cu. Both bulk ZnO:Cu and quantum dots (QDs) of ZnO doped with Cu were experimentally investigated. The most characteristic optical feature of Cu is the so-called structured green emission (SGE) with the zero phonon line at 2.859 eV, multiple LO phonon replicas, and hyperfine splitting due to the two Cu isotopes, as first observed in the seminal work of Dingle [1]. Numerous optical, magnetooptical and EPR measurements assessed that SGE is due to isolated substitutional Cu.

Surprisingly, however, in spite of the experimental and theoretical effort, the mechanism of SGE is still controversial (see e.g. [1, 2, 3]) regarding the relevant charge state of Cu, the Cu levels involved in the transition, and the origin of the fine structure of SGE. To explain the origin of SGE, we performed the LDA+U calculations using the Quantum Espresso code for both bulk and a 200-atom ZnO:Cu QD. Spin polarization was taken into account. The +U terms applied to p(O) and d(Zn) orbitals provide excellent band structure of ZnO, and the correct band gap of small QDs. The +U term for d(Cu) is considered as a fitting parameter. The energy levels and magnetic moments were calculated for Cu^{3+}, Cu^{2+} and Cu^{+} charge states.

The mechanism of SGE is assessed by calculating the probabilities of possible optical transitions between Cu levels and ZnO bands. The obtained results demonstrate that (i) SGE follows from the allowed transition between the Cu^{+} level and a free hole, (ii) the observed fine ~10 meV splitting of the 2.859 eV line is due to the splitting of the valence band top of ZnO, (iii) the luminescence at 0.72 eV (which was not considered previously by theory) is due to the intracenter transition, and (iv) the expected luminescence at 2.0 eV is not observed since it is forbidden by selection rules. The obtained photoluminescence energies are in excellent agreement with experimental data.

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